

Statistical Mechanics of Vibration-Induced Compaction of Powders

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Abstract

We propose a theory which describes the density relaxation of loosely packed, cohesionless granular material under mechanical tapping. Using the compactivity concept we develop a formalism of statistical mechanics which allows us to calculate the density of a powder as a function of time and compactivity. A simple fluctuation-dissipation relation which relates compactivity to the amplitude and frequency of a tapping is proposed. Experimental data of E.R.Nowak *et al.* [*Powder Technology* **94**, 79 (1997)] show how density of initially deposited in a fluffy state powder evolves under carefully controlled tapping towards a random close packing (RCP) density. Ramping the vibration amplitude repeatedly up and back down again reveals the existence of reversible and irreversible branches in the response. In the framework of our approach the reversible branch (along which the RCP density is obtained) corresponds to the steady state solution of the Fokker-Planck equation whereas the irreversible one is represented by a superposition of "excited states" eigenfunctions. These two regimes of response are analyzed theoretically and a qualitative explanation of the hysteresis curve is offered.

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I. INTRODUCTION

There is an increasing interest in applying the methods of statistical mechanics and kinetic theory to granular materials where processes are dominated by geometrical constraints and friction, and initially posses a memory of sample's preparation [1,2].

In this paper we propose an analytical approach which gives a qualitative explanation of experimental data obtained by Nowak *et al.* [3]. They have shown that external vibrations lead to a slow, approach of the packing density to a final steady-state value. Depending on the initial conditions and the magnitude of the vibration acceleration, the system can either reversibly move between steady-state densities or can become irreversibly trapped into metastable states that is the rate of compaction and the final density depend sensitively on the history of vibration intensities that the system experiences (see Fig.1).

A granular material is a system with a large number of individual grains and therefore it has a huge number of degrees of freedom. Grains interact with each other via contact forces which are determined by friction, gravitational loading and amplitude of an external force if the system is perturbed. Therefore one needs to invent a formalism that would allow us to calculate macroscopic averages in terms of microscopic (i.e. of individual grains) properties of the system. If we assume that it may be characterised by a small number of parameters (e.g. analogous to temperature) and that this system has properties which are reproducible given the same set of extensive operations (i.e. operations acting upon the system as a whole rather than upon individual grains) then we may apply the ideas of statistical averaging over the ensemble of configurations to granular systems [4].

In the present paper we consider the simplest model of a granular material by introducing the volume function W and assume the simplest case that all configurations of a given volume are equally probable; in many cases the mechanism of deposition will leave a history in the configuration but this will not be considered here. W will depend on the coordinates of the grains and their orientations and is the analogue of a Hamiltonian. Averaging over all the possible configurations of the grains in real space gives us a configurational statistical ensemble describing the random packing of grains. Since we are assuming that we are dealing with a system whose constituents are hard (i.e. impenetrable) we have to include some account of this in our formalism in order to reduce the number of possible configurations the system may occupy. Also for a packing which is stable under applied force we must consider the configurations restricting the number of possible volume states that the system may occupy to be only those configurations which are stable. Also grains cannot overlap and this condition produces very strong constraints (frustration) on their relative positions. This implies that all grains have to be in contact with their nearest neighbours. Of course in the real powder the topological defects can exist such as vacancies, voids or arches. But as these will be a subject of a future paper we do not consider them here. Thus we have a "microcanonical" probability distribution [4]:

$$P = e^{-\frac{S}{\lambda}} \delta(V - W) \Theta(\text{contacts}) \quad (1)$$

$$e^{\frac{S}{\lambda}} = \int \delta(V - W) \Theta(\text{contacts}) d(\text{all degrees of freedom}) \quad (2)$$

where we define Θ as:

$$\Theta(\text{contacts}) = \begin{cases} 1 & \text{if } z \geq z_m \\ 0 & \text{if } z < z_m \end{cases}$$

where z_m is the minimal coordination number of a grain [5]. We have to introduce Θ because we consider the stable isotropic and homogeneous packings. Just as in conventional statistical mechanics with microcanonical distribution:

$$P = e^{-\frac{S}{k}} \delta(E - H) \quad (3)$$

and temperature:

$$T = \frac{\partial E}{\partial S} \quad (4)$$

we can define the analogue of temperature as:

$$X = \frac{\partial V}{\partial S}. \quad (5)$$

This fundamental parameter is called compactivity [4]. It characterises the packing of a granular material and may be interpreted as being characteristic of the number of ways it is possible to arrange the grains in the system into volume ΔV such that the disorder is ΔS . Consequently the two limits of X are 0 and ∞ , corresponding to the most and least compact stable arrangements. This is clearly a valid parameter for sufficiently dense powders because one can in principle calculate the configurational entropy of an arrangement of grains and therefore derive the compactivity from the basic definition [6]. One can expect despite the strong constraints resulting from the stability conditions, the number of packings to grow exponentially with the volume of a sample and the configurational entropy defined as a logarithm of this number is extensive.

As usual it is more convenient to introduce the canonical probability distribution:

$$P = e^{\frac{Y-W}{\lambda X}}, \quad (6)$$

where λ is a constant which gives the entropy the dimension of volume, Y we call the effective volume, it is the analogue of the free energy:

$$e^{-\frac{Y}{\lambda X}} = \int e^{-\frac{W(\mu)}{\lambda X}} d(\text{all}), \quad V = Y - X \frac{\partial Y}{\partial X}. \quad (7)$$

To illustrate this theory consider the simplest example of a W , the analogue of Bragg-Williams approximation [4]: each grain has neighbours touching it with a certain coordination and angular direction. In order to set up an analogy with the statistical mechanics of alloys we assume that each grain has a certain property, which defines the “interaction” with its nearest neighbours. Taking the coordination number of a grain as such a property and assuming that there are just two types of coordination z_0 and z_1 we assign a volume v_i to any grain with z_i coordination number. Thus we write the volume function as:

$$W = n_0 v_0 + (N - n_0) v_1 \quad (8)$$

where N is the number of grains in the system, n_i is the number of grains with the coordination number z_i and $N = n_0 + n_1$. The simple calculation of Y and V gives us [4]:

$$Y = N \frac{(v_0 + v_1)}{2} - N \lambda X \ln 2 \cosh \frac{(v_0 - v_1)}{\lambda X} \quad (9)$$

$$V = N \frac{(v_0 + v_1)}{2} + N \frac{(v_0 - v_1)}{2} \tanh \frac{(v_0 - v_1)}{\lambda X}. \quad (10)$$

Thus we have two limits: $V = Nv_0$, when $X \rightarrow 0$ and $V = N(v_0 + v_1)/2$ when $X \rightarrow \infty$ (N is a number of grains). Note that the maximum V is not Nv_1 just as in the thermal system (say a spin in a magnetic field) with two energy levels E_0 and E_1 one has $E = E_0$ when $T \rightarrow 0$ and $E = (E_0 + E_1)/2$ when $T \rightarrow \infty$.

II. "TWO-VOLUMES" MODEL: SOLUTION OF THE FOKKER-PLANCK EQUATION

We consider the rigid grains powder dominated by friction deposited in a container which will be shaken or tapped (in order to consider the simplest case we ignore other possible interactions e.g. cohesion and do not distinguish between the grain-grain interactions in the bulk and those on the boundaries). We assume that most of the particles in the bulk do not acquire any non ephemeral kinetic energy i.e. the change of a certain configuration occurs due to continuous and cooperative rearrangement of a free volume between the neighbouring grains. Any such powder will have a remembered history of deposition and in particular can have non-trivial stress patterns, but we will confine the analysis of this paper to systems with homogeneous stress which will permit us to ignore it. The fundamental assumption is that under shaking a powder can return to a well defined state, independent of its starting condition. Thus in the simplest system, a homogeneous powder, the density characterises the state.

It is sensible to seek the simplest algebraic model for our calculation and to this end since the orientation of the grain must have at least two degrees of freedom, say μ_1 and μ_2 , our volume function is:

$$W = v_0 + (v_1 - v_0)(\mu_1^2 + \mu_2^2) \quad (11)$$

implying a two-dimensional picture (see Fig.2). When $\mu = 0$ we have $W = v_0$ then the grain is "well oriented" which means that a free volume is minimal and when $\mu = 1$ and $W = v_1$ then the grain is "not well oriented" (free volume is maximal). It is a self-consistent approximation since the parameters v_0 and v_1 are the average volumes of the grain in the presence of other grains. In general we can write:

$$e^{-\frac{Y}{\lambda X}} = \int w(\mu) e^{-\frac{W(\mu)}{\lambda X}} d\mu \quad (12)$$

where $w(\mu)$ is the weight factor attached to μ . From (7) we derive Y and V :

$$Y = Nv_0 - N \lambda X \ln \left\{ \frac{\lambda X}{v_1 - v_0} (1 - e^{-\frac{v_1 - v_0}{\lambda X}}) \right\} \quad (13)$$

$$V = N(v_0 + \lambda X) - \frac{N(v_1 - v_0)}{e^{\frac{v_1 - v_0}{\lambda X}} - 1}. \quad (14)$$

Thus we have the same limits as for volume function (8): $V = Nv_0$, when $X \rightarrow 0$ and $V = N(v_0 + v_1)/2$ when $X \rightarrow \infty$.

The main physical idea of our approach is the following: all grains in the bulk experience the external perturbation as a random force with zero correlation time so that the process of compaction can be seen as the Ornstein-Uhlenbeck process for the degrees of freedom μ_i , $i = 1, 2$ [7]. Therefore we write the Langevin equation:

$$\frac{d\mu_i}{dt} + \frac{1}{\nu} \frac{\partial W}{\partial \mu_i} = \sqrt{D} f_i(t) \quad (15)$$

where $\langle f_i(t) f_j(t') \rangle = 2\delta_{ij} \delta(t - t')$ and ν characterises the frictional resistance imposed on the grain by its nearest neighbours. The term $f_i(t)$ on the RHS of (15) represents the random force generated by a tap. The terms "shaken" or "tapped" have been used above and we have to make them more precise. The derivation gives the analogue of the Einstein relation that $\nu = (\lambda X)/D$. If we identify f with the amplitude of the force a used in the tapping, the natural way to make this dimensionless is to write the "diffusion" coefficient as :

$$D = \left(\frac{a}{g}\right)^2 \frac{\nu \sigma^2}{v} \quad (16)$$

That is we have a simplest guess for a fluctuation-dissipation relation:

$$\lambda X = \left(\frac{a}{g}\right)^2 \frac{\nu^2 \sigma^2}{v} \quad (17)$$

where v is the volume of a grain, σ the frequency of a tap and g the gravitational acceleration. Use of the Langevin equation (11) is of course a crude simplification as it does not explicitly take into account the presence of boundaries and topological constraints. Generally speaking one would have to use the integro-differential Langevin equation with the memory kernel:

$$\frac{d\mu_i}{dt} + \int_0^t K(t - t') \mu_i(t') dt' = \sqrt{D} f_i(t), \quad (18)$$

as one sees in experiment that the final density depends sensitively on the history of vibration intensities. Clearly to solve such an equation is not a trivial task although the solution could give us the better understanding of many interesting features of granular compaction. The problem of how to choose the initial values of μ is in reality the deposition problem. We discuss it later.

The Langevin equation can be easily solved for W quadratic in μ :

$$\mu_i(t) = \mu_i(0)e^{-\gamma t} + \sqrt{D}e^{-\gamma t} \int_0^t f(t')e^{\gamma t'} dt' \quad (19)$$

Averaging over the ensemble we get:

$$\langle \mu_i(t) \rangle = \mu_i(0)e^{-\gamma t} \quad (20)$$

where $\mu_i(0) = 1$ is the initial value of μ_i , $\gamma = 2\frac{(v_1-v_0)}{\nu}$ has the meaning of relaxation time of the degree of freedom μ . As $t \rightarrow \infty$ μ goes to $\mu_f = 0$ which corresponds to the random close packing limit. The Fokker-Planck equation seems to be quite generic in modelling the response of granular materials to an externally applied shear rate [8] although in that problem it is more convenient to use the volume “Hamiltonian” W as a function of the coordination number of each grain. The standard treatment of the Langevin equation (15) is to use it to derive the Fokker-Planck equation:.

$$\frac{\partial P}{\partial t} = \left(D_{ij} \frac{\partial^2}{\partial \mu_i \partial \mu_j} + \gamma_{ij} \frac{\partial}{\partial \mu_i} \mu_j \right) P = 0 \quad (21)$$

where $D_{ij} = D\delta_{ij}$ and $\gamma_{ij} = \gamma\delta_{ij}$. Equation (21) can be solved explicitly. It has right- and left-hand eigenfunctions P_n and Q_n and eigenvalues ω_n such that:

$$\omega_n P_n = \frac{\partial}{\partial \mu_j} \left(D_{ij} \frac{\partial}{\partial \mu_i} + \gamma_{ij} \mu_j \right) P_n \quad (22)$$

$$\omega_n Q_n = \left(-D_{ij} \frac{\partial}{\partial \mu_i} + \gamma_{ij} \mu_j \right) \frac{\partial}{\partial \mu_j} Q_n \quad (23)$$

or equivalently a Green function:

$$G = \sum_n P_n(\mu) Q_n(\mu) e^{-\omega_n t}. \quad (24)$$

It follows that if we start with a non-equilibrium distribution:

$$P^{(0)}(t=0) = \sum_{n=0}^{\infty} A_n P_n, \quad A_n = \int Q_n P^{(0)} d\mu_1 d\mu_2 \quad (25)$$

and it will develop in time as:

$$P^{(0)}(t) = A_0 P_0 + \sum_{n \neq 0}^{\infty} A_n P_n e^{-\omega_n t} \quad (26)$$

where $\int P^{(0)} d\mu_1 d\mu_2 = A_0$. This coefficient is determined by a number of grains present in the powder, hence must be a constant. The steady-state distribution function is:

$$P^{(0)}(t \rightarrow \infty) = \frac{e^{-\frac{(v_1-v_0)(\mu_1^2+\mu_2^2)}{\lambda X}}}{\int_0^1 e^{-\frac{(v_1-v_0)(\mu_1^2+\mu_2^2)}{\lambda X}} d\mu_1 d\mu_2} \quad (27)$$

The Fokker-Planck operator (21) has a complete orthogonal set of eigenfunctions:

$$P_n = H_n e^{-\frac{(v_1-v_0)(\mu_1^2+\mu_2^2)}{\lambda X}} \quad (28)$$

where H_n are Hermite polynomials and $\mu_i \in (0, \infty)$. In our case $\mu_i \in (0, 1)$. One can avoid this mathematical difficulty, taking into account the crudety of our model and

constructing the “first excited state”: $P_2 = (a(\mu_1^2 + \mu_2^2) + b) e^{-\frac{(v_1 - v_0)(\mu_1^2 + \mu_2^2)}{\lambda X}}$ orthogonal to the ground-state eigenfunction P_0 . This eigenfunction describes the initial state of our system i.e. loosely packed deposited powder. Therefore it is easy to see the initial non-equilibrium distribution (26) depends on how the powder is deposited. Constants a and b can be defined from the orthonormality relations. By using:

$$P_n = Q_n P^{(0)}(t \rightarrow \infty), \quad Q_0 = 1 \quad (29)$$

and:

$$\int_0^1 Q_2 \hat{L}_{FP} P_2 d\mu_1 d\mu_2 = \omega_2 \quad (30)$$

one can easily verify that the eigenvalue ω_2 (which corresponds to P_2 and gives us the decay rate of our nonequilibrium distribution) is a constant dimensionless number.

Suppose now that deposition produces a highly improbable configuration, indeed the most improbable configuration whith: $\mu_1^2 + \mu_2^2 = 2$ and the mean volume function is $\bar{W} = 2v_1 - v_0 \approx v_1$, where:

$$\bar{W}(X, t) = \int P^{(0)}(X, t) W d\mu_1 d\mu_2. \quad (31)$$

It is possible to imagine a state where all the grains are improbably placed, i.e. where each grain has its maximum volume v_1 . In a thermal analogy this would be like fully magnetised magnetic array of spins where the magnetic field is suddenly reversed. Such a system is highly unstable and equilibrium statistical mechanics does not cover this case at all. It will thermalize consuming the very high energy whilst establishing the appropriate temperature. Powders however are dominated by friction, so if one could put together a powder where the grains were placed in high volume configuration, it will just sit there until shaken; when shaken it will find its way to the distribution (6). It is possible to identify physical states of the powder with characteristic values of volume in our model. The value $V = Nv_1$ corresponds to the “deposited” powder, i.e. the powder is put into the most unstable condition possible, but friction holds it. When $V = Nv_0$ the powder is shaken into closest packing. The intermediate value of $V = (v_0 + v_1)/2$ corresponds to the minimum density of the reversible curve. Thus we can offer an interpretation of three values of density presented in the experimental data [3].

The general solution of the Fokker-Planck equation (21) goes to its steady-state value when $t \rightarrow \infty$ so we can expect $\bar{W}(X, t)$ to diminish (as the amplitude of tapping increases) until one reaches the steady-state value $\bar{W}(X)$. The formula (14) can be obtained using (31) when $t \rightarrow \infty$ and represents a reversible curve in experimental data of [3]: altering a moves one along the curve $\rho = \frac{v}{\bar{W}(X)} = \rho(a)$. We can identify time with the number of taps, so wherever we start with any initial $\rho_{(0)}$ and a , successive tapping takes one to reversible curve $\rho(a)$. Or, if one decides on a certain number of taps, $t \neq \infty$, one will traverse a curve $\rho_t(a)$, where $\rho_\infty(a) = \rho(a)$. Notice that the simple result lies within the crudety of our model. The general problem will not allow us to think of X as $X(a)$ independent of the development of the system. The thermal analogy is this: if the Brownian motion in an ensemble of particles is controlled by a random force f which is defined in terms of its amplitude and time profile, this random force defines the temperature in the system. Our problem is like a magnetic system where magnetic dipoles are affected by a constant magnetic field, being random at high temperature, and increasingly oriented by the external field as the temperature falls.

III. DISCUSSION

The physical picture presented in section 2 is consistent with everyday knowledge of granular materials: when poured they take up a low density but when shaken settle down, unless shaken violently when they return to low density. These effects are much more pronounced in systems with irregularly shaped grains than with fairly smooth uniform spheres, indeed the more irregular a grain is, the more the discussion above describes big differences between $\rho_{(0)}$ and ρ . The experimental data of [3] show the packing density dependence on parameter $\Gamma = a/g$ for a fixed number of taps. A loosely packed bead assembly first undergoes irreversible compaction corresponding to the lower branch of $\rho(\Gamma)$. The settling behavior becomes reversible only once a characteristic acceleration has been exceeded. Our theory gives three points $\rho(X = 0)$, $\rho(X = \infty)$ and $\rho(t = 0)$ which are in the ratio: v_0^{-1} , $\frac{2}{(v_0+v_1)}$, v_1^{-1} and these are in reasonable agreement with experimental data: $\rho(X = 0) = \frac{1}{v_0} \approx 0.64$, $\rho_0 = \frac{1}{v_1} \approx 0.58$ and $\rho(X = \infty) = \frac{2}{(v_0+v_1)} \approx 0.62$. Another important issue is the validity of the compactivity concept for a “fluffy” but still mechanically stable granular arrays e.g. for those composed of spheres with $\rho \leq 0.58$. In our theory $\rho(X = \infty)$ corresponds to the beginning of the reversible branch (see Fig.1) and using our analogy with a magnetic system is analogous to dipoles at a high temperature. The irreversible branch has an analogue in the behaviour of the magnetic system where initially the dipoles are strongly aligned with an external field but this field is then flipped to the opposite direction.

The fluffy powder is a very complicated object as it has plenty of topological defects and stress arches. Throughout the paper we assumed that our granular array is spatially homogeneous which is the case for densities of the reversible curve. However this is a very subtle problem which will be a subject of a future paper. It is a difficult problem to decide whether embarking on a vast amount of algebraic work that a superior mode would entail is worthwhile. But our simple model is quite physical and can be extended when experiments would justify the work.

A final point is that we find the lower (irreversible) curve build up to the upper (reversible) curve exponentially in time:

$$V(t) = V_{\text{initial}} e^{-\omega t} + V_{\text{final}}(1 - e^{-\omega t}) \quad (32)$$

while one can expect the logarithmic in time approach to the steady state density e.g. the Vogel-Fulcher type curve which is typical of disordered thermal systems such as spin and structural glasses [9]

$$V(t) = V_f + (V_i - V_f)e^{-\omega t} + Tt^{-\epsilon} \quad (33)$$

where ϵ is large.

In fact, identifying t with the number of taps n , the law seems to be even slower at $(\ln t)^{-1}$. Our simple analysis is clearly inadequate to obtain such a result which is quite outside the straightforward method of expansion in the present set of eigenfunctions. However there is an argument by de Gennes [10] which argues that a Poisson distribution can provide this logarithmic behaviour.

IV. ACKNOWLEDGEMENT

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FIGURES

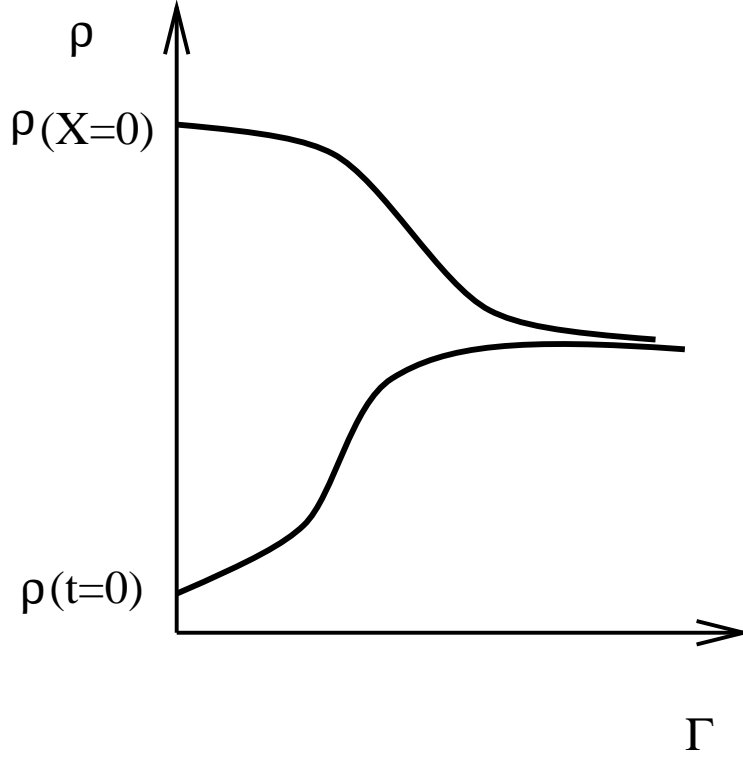


FIG. 1. Dependence of the steady-state packing density on the tapping history (Nowak et al.). Experimental values of density packing fraction are in the following correspondence with model parameters: $\rho(X = 0) = \frac{1}{v_0} \approx 0.64$, $\rho(t = 0) = \rho_0 = \frac{1}{v_1} \approx 0.58$ and $\rho(X = \infty) = \frac{2}{(v_0 + v_1)} \approx 0.62$.

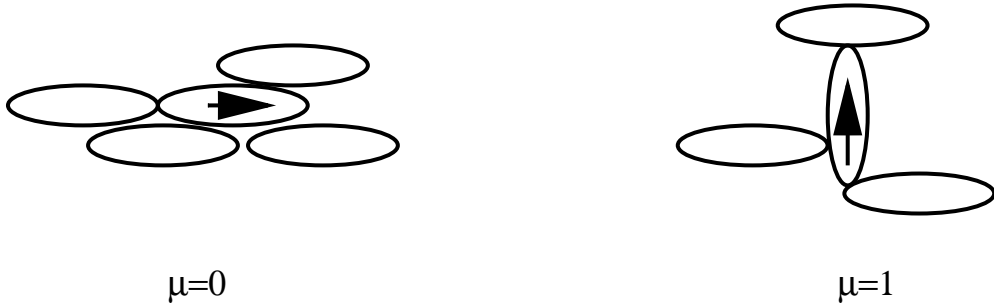


FIG. 2. Graphical representation for the limit values of the degree of freedom μ in 2-D